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(54) PRODUCTION OF CORDIERITE-BASED CERAMIC HONEYCOMB STRUCTURE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for producing a cordiertie-based ceramic honeycomb structure, making it possible to thin the walls of the structure and enhance the density of the cells of the structure, and capable of contributing to the improvement of moldability (especially flowability and shape retainability), mechanical strength (hydrostatic pressure breaking strength) and catalyst-carrying characteristics when extrusion-molded.
SOLUTION: This method for producing a cordierite-based ceramic honeycomb structure wherein the main component of the crystal phase is cordierite comprises adding and kneading a molding auxiliary to cordierite raw materials, extrusion-molding the obtained raw material batch, drying the molded product and then calcining the dried product. Therein, the cordierite raw material batch for the extrusion-molding contains ≥65 wt.% of cordierite raw materials which comprise talc, kaolin, and aluminum hydroxide and has crystal water, and the kaolin having an average particle diameter of ≥5 μm and a BET specific surface area of ≤10 m2/g is contained in an amount of ≥10 wt.%.

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* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] By fabricating and drying by extrusion molding and subsequently calcinating this raw material batch, after carrying out addition kneading of the shaping assistant and considering as a raw material batch at a cordierite-ized raw material It is the approach of manufacturing the honeycomb structure object whose principal component of a crystal phase is cordierite. In the cordierite-ized raw material batch for extrusion molding, talc, a kaolin, The cordierite metaplasia raw material which has the water of crystallization which consists of an aluminum hydroxide is contained 65% of the weight or more. And the manufacture approach of the nature of cordierite ceramic honeycomb structure object characterized by blending the kaolin whose mean particle diameter is 5 micrometers or more, and whose BET specific surface area is below 10m2/g 10% of the weight or more.
[Claim 2] The manufacture approach of a nature of cordierite ceramic honeycomb structure object according to claim 1 that the value of the mean diameter/BET specific surface area of a kaolin is one or more.
[Claim 3] The manufacture approach of the nature of cordierite ceramic honeycomb structure object according to claim 1 or 2 using the cordierite-ized raw material which classified under in the septum thickness of an extrusion dice in the cordierite-ized raw material batch.
[Claim 4] The manufacture approach of a nature of cordierite ceramic honeycomb structure object given in any 1 term of claims 1-3 to which slit width uses an extrusion dice 110 micrometers or less at the time of extrusion molding.
[Claim 5] The manufacture approach of a nature of cordierite ceramic honeycomb structure object given in any 1 term of claims 1-4 24 - 38% and whose AISO static reinforcement porosity is 10kg/cm2 or more while the coefficient of thermal expansion for 40-800 degrees C of the direction of passage of a nature of cordierite ceramic honeycomb structure object is less than [0.8x10-6/degree C].

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the approach of carrying out extrusion molding of the nature of cordierite ceramic honeycomb structure object, and manufacturing it.
[0002]
[Description of the Prior Art] The nature of cordierite ceramic honeycomb structure object is used as an automobile and industrial emission-gas-purification catalyst support, a filter, a heat exchange object, etc. Since there are the improvement in on the strength for the formation of low-voltage force loss for contraction of the volume of the ceramic honeycomb catalyst support especially used for the exhaust-gas equipment for automobiles, i.e., the improvement in the catalyst engine performance, improvement in the light off engine performance, fuel-consumption engine-performance amelioration, and the improvement in an output of an engine and the cost cut of canning to casing and the need of installing near the engine in order to raise catalytic activity further, with the advance of a technology in recent years, improvement in thermal shock resistance and improvement in reinforcement were desired strongly.
[0003] For this reason, although thin wall-ization of the rib of a honeycomb structure object has been considered conventionally, with the cel consistency for the formation of a thin wall of the rib of the honeycomb structure object for the improvement in the catalyst engine performance, the formation of a high cel consistency, and the formation of low voltage force loss maintained the fall of the reinforcement by the formation of a thin wall of a porous nature of cordierite ceramic honeycomb structure object, and the mouthpiece at the time of extrusion molding -- since it was necessary to atomize a use raw material (especially source raw material of a magnesia) by reduction in slit width, there was a problem accompanied by the rise of a large coefficient of thermal expansion.
[0004] Moreover, the eburnation of the cordierite ceramics is difficult, and on the cordierite base which shows low expansibility as the coefficient of thermal expansion from a room temperature to 800 degrees C indicates less than [2.0x10-6/degree C] to be especially, since it needs to limit the amount of impurities which should serve as a fusing agent like calcia, alkali, and soda very a little, its glass phase decreases very much and it serves as a porous body.
[0005] Especially the nature of cordierite ceramic honeycomb structure object used as catalyst support for automobile exhaust purification in recent years Since the coefficient of thermal expansion from a room temperature to 800 degrees C needs that it is less than [1.5x10-6/degree C], Even if it uses raw materials, such as talc with few impurities selected carefully, a kaolin, and an alumina It did not pass over porosity to the thing of at most 20 - 45% of range, and especially, with the honeycomb structure object of 30% or less of porosity, the increment in the amount of impurities and the atomization of a raw material are required, and, as for the following [1.0x10-6/degree C], the coefficient of thermal expansion to 800 degrees C was not obtained from a room temperature.
[0006] Furthermore, in the nature honeycomb structure object of cordierite of comparatively low porosity, since desiccation and contraction at a baking process were large, it was difficult to be easy to generate a crack and to manufacture the honeycomb structure object of a big dimension with the sufficient yield.
[0007] In order to cancel these, in JP,4-70053,B, the approach of making eburnation of the porosity of the cordierite ceramics 30% or less, and making the ceramic itself high intensity is indicated. According to deformation of the honeycomb cel produced at the time of extrusion molding, in order to prevent the fall of the AISO static reinforcement which is a compressive load from the outer wall and the direction of a periphery of a honeycomb structure object, by making the porosity of the cordierite ceramics 30% or less, this carries out eburnation of the ceramic itself, and high-intensity-izes it.

[0008] However, by the above-mentioned approach, since the porosity of the cordierite ceramics was 30% or less, while being unable to desire improvement in the catalyst support property of a nature of cordierite ceramic honeycomb structure object, the moldability at the time of extrusion molding was not good, and was not able to say that it was enough about the formation of a thin wall of a nature of cordierite ceramic honeycomb structure object, and high cel consistency-ization, either.
[0009]
[Problem(s) to be Solved by the Invention] therefore, the place which this invention be make in view of the above-mentioned conventional technical problem, and be make into the purpose offer the manufacture approach of the nature of cordierite ceramic honeycomb structure object which can be contribute to improvement in the formation of a thin wall of a nature of cordierite ceramic honeycomb structure object and the moldability at the time of extrusion molding (especially a fluidity and firmness), a mechanical strength (hydrostatic pressure disruptive strength), and a catalyst support property while being able to form a high cel consistency.
[0010]
[Means for Solving the Problem] Namely, by fabricating and drying by extrusion molding and subsequently calcinating this raw material batch, after according to this invention carrying out addition kneading of the shaping assistant and considering as a raw material batch at a cordierite-ized raw material It is the approach of manufacturing the honeycomb structure object whose principal component of a crystal phase is cordierite. In the cordierite-ized raw material batch for extrusion molding, talc, a kaolin, The cordierite metaplasia raw material which has the water of crystallization which consists of an aluminum hydroxide is contained 65% of the weight or more. And the manufacture approach of the nature of cordierite ceramic honeycomb structure object characterized by blending the kaolin whose mean particle diameter is 5 micrometers or more, and whose BET specific surface area is below 10m2/g 10% of the weight or more is offered. At this time, it is desirable that the value of the mean particle diameter/BET specific surface area of a kaolin is one or more.
[0011] Moreover, it is desirable to use the cordierite-ized raw material which classified under in the septum thickness of an extrusion dice in a cordierite-ized raw material batch in this invention.
[0012] Furthermore, while the coefficient of thermal expansion for 40-800 degrees C of the direction of passage of a nature of cordierite ceramic honeycomb structure object is less than [0.8x10-6/degree C] in this invention, it is desirable that porosity is [24 - 38% and AISO static reinforcement] 10kg/cm2 or more.
[0013]
[Embodiment of the Invention] The manufacture approach of the nature of cordierite ceramic honeycomb structure object of this invention is to contain the cordierite metaplasia raw material which has the water of crystallization which consists of talc, a kaolin, and an aluminum hydroxide into the cordierite-ized raw material batch for extrusion molding 65% of the weight or more. Thereby, the fluidity of the plastic matter at the time of extrusion molding and the firmness of the honeycomb Plastic solid after extrusion molding can be improved.
[0014] As mentioned above, it is important to use three sorts of raw raw materials, talc, a kaolin, and an aluminum hydroxide, for coincidence as a cordierite metaplasia raw material by the manufacture approach of the nature of cordierite ceramic honeycomb structure object of this invention. Moreover, in order that that the content of the cordierite metaplasia raw material in a cordierite-ized raw material batch is 70 % of the weight or more more preferably 65% of the weight or more may prevent the rise of the extrusion pressure at the time of extrusion molding and it may raise the firmness after extrusion molding, it is desirable. Furthermore, since increase in quantity of temporary-quenching talc, a temporary-quenching kaolin, and an alumina becomes the cause of degrading the fluidity of a plastic matter remarkably, it is desirable to make it necessary minimum.
[0015] However, although the cordierite metaplasia raw material is suitable to carry out extrusion molding of the thin wall honeycomb structure object without cel deformation, it causes [of the baking crack of a nature of cordierite ceramic honeycomb structure object] generating.
[0016] For this reason, it is important to blend with a cordierite-ized raw material batch the kaolin whose mean diameter is 5 micrometers or more and whose BET specific surface area is below 10m2/g 10% of the weight or more by the manufacture approach of the nature of cordierite ceramic honeycomb structure object of this invention. Thus, since necessary minimum of the water ratio required in order to obtain the plastic matter in which extrusion is possible by blending with a cordierite-ized raw material batch the kaolin which has the above-mentioned property can be carried out, seemingly, the volume fraction of a particle becomes large and can shorten distance between particles. In an extrusion-molding process, since the plastic matter

produced as mentioned above can shorten time amount which recovery (re-condensation) takes when wide opened from shearing once it receives distortion by shearing, it can raise the firmness of a Plastic solid. At this time, it is desirable that the value of the mean particle diameter/BET specific surface area of a kaolin is one or more.

[0017] Since the viscosity of a dispersed system becomes high on the other hand so that surface energy is high when it has the high BET specific surface area (excess of 10m2/g) whose kaolin blended with a cordierite-ized raw material batch is a particle (less than 5 micrometers), A water ratio required in order to obtain the plastic matter in which extrusion is possible increases, seemingly, the volume fraction of a particle becomes small, the distance between particles increases, and it sets at an extrusion-molding process. Once receiving distortion by shearing, the time amount which the recovery (re-condensation) when being wide opened from shearing takes will become long, and the firmness of a Plastic solid will fall.

[0018] The above-mentioned kaolin moreover, by blending with a cordierite-ized raw material batch 15 to 25% of the weight more preferably 10% of the weight or more Since it is an inorganic electrolyte and an end face can reflect greatly the property of a kaolin that stripped planes are the just charged unique fine particles in the rheology property of a plastic matter, under existence of water negative, In an extrusion-molding process, in the state of high shear at the time of passing through an extrusion dice, it is easier to deform, and the suitable plastic matter which cannot deform easily can be obtained in the condition of having been wide opened from ** which is not carried after passing through an extrusion dice.

[0019] Moreover, as for the cordierite-ized raw material batch used by this invention, it is desirable to use the cordierite-ized raw material which classified under in the septum thickness of an extrusion dice. It can prevent getting it blocked in the slit of an extrusion dice by this, and the good Plastic solid which does not have a deficit in the rib of a honeycomb can be acquired.

[0020] In addition, as for the talc used from the cordierite metaplasia raw material of this invention, it is desirable that it is small micro talc of microcrystal (single crystal). Moreover, as for an aluminum hydroxide, what is the high BET specific surface area by which grinding processing was carried out with the Bayer process after a crystal deposit and for lamination is desirable. Here, a BET specific surface area is the approach of saying the surface area per unit mass of the solid-state for which it asked from the gas adsorption theory (BET isotherm) of Brunauer, Emett, and Teller, calculating the area of a multilayer, and determining surface area.

[0021] Furthermore, it is desirable that the coefficient of thermal expansion for 40-800 degrees C of the nature of cordierite ceramic honeycomb structure object acquired by this invention is less than [0.8x10-6/degree C] in the direction of passage. This is because the thermal shock resistance [Esp] of a cylinder-like honeycomb structure object (diameter of about 100mm) is less than 700 degrees C and use of the exhaust gas catalyst support for automobiles cannot be borne, if a coefficient of thermal expansion [CTE] (the direction of passage of a honeycomb baking object) exceeds 0.8x10-6/degree C.

[0022] Next, the manufacture approach of the nature of cordierite ceramic honeycomb structure object of this invention is explained to a detail. The cordierite-ized raw material batch of the nature honeycomb structure object of cordierite prepares the cordierite metaplasia raw material which consists of talc, a kaolin, and an aluminum hydroxide, and it prepares the remainder with a temporary-quenching kaolin, an alumina, a silica, temporary-quenching talc, etc. 65% of the weight or more so that the chemical composition of a principal component may become 2:42 - 56 % of the weight of SiO(s), 2O3:30 - 45 % of the weight of aluminum, and MgO:12-16% of the weight. An organic binder and plasticizers, such as water and methyl cellulose, were added to this cordierite-ized raw material batch, and the honeycomb Plastic solid was fabricated after mixing / kneading using extrusion molding. Next, a nature of cordierite ceramic honeycomb structure object (honeycomb baking object) can be acquired by drying a honeycomb Plastic solid and calcinating at the temperature of 1350-1440 degrees C.

[0023] Since the plastic matter which was excellent in the fluidity at the time of extrusion molding by carrying out specified quantity (10 % of the weight or more) combination of the kaolin whose mean particle diameter is 5 micrometers or more, and whose BET specific surface area is below 10m2/g at this time, and also has the firmness over the self-weight deformation after extrusion molding is obtained, a thin wall and the honeycomb structure object of a high cel consistency (for example, wall thickness: 40 micrometers, cel consistency:200 cel / cm2) can be manufactured. Moreover, while there are very few coefficients of thermal expansion of the honeycomb baking object after cel deformation of the honeycomb Plastic solid after extrusion molding and baking by manufacturing a thin wall honeycomb structure object as mentioned above and being able to make AISO static reinforcement in the honeycomb baking object of 24 - 38% of porosity into 10kg/cm2 or more, when porosity is 30% or more, a catalyst support property can also be raised.

[0024] In addition, in order to prevent the crack initiation of a nature of cordierite ceramic honeycomb structure object honeycomb structure object, it is desirable to control to below 50 degrees C / Hr, and even if the programming rate in the water-of-crystallization dehydration temperature field of an aluminum hydroxide and a kaolin performs debinder processing before baking, it is effective.
[0025]
[Example] Although this invention is further explained to a detail based on an example, this invention is not restricted to these examples. In addition, the cordierite-ized raw material, honeycomb Plastic solid, and honeycomb baking object which were acquired by each example evaluated the engine performance by the approach shown below.
[0026] (Fluid measuring method of a plastic matter) After measuring the knockout speed of the honeycomb when extruding a plastic matter by a certain specific plunger pressure from the extrusion dice (mouthpiece) of 100 micrometers of slit thickness, from the pressure, extrusion speed, and the thickness of a slit, the shear rate at the time of extrusion dice passage was calculated, and the value was converted into the apparent viscosity (MPa-s). The fluidity of that plastic matter becomes the outstanding thing, so that this apparent viscosity (fluid index viscosity) is small.
[0027] (Measuring method of the firmness of a honeycomb Plastic solid) A plastic matter is extruded from a plunger, it considers as the solid object of fixed magnitude (25mmphix30mmL), and the load load (kgf) when compressing by compression velocity 1 mm/s using an autograph is measured. It saw from the stress-strain curve at this time, and calculation and an apparent viscosity (MPa-s) were computed for Young's modulus (inclination in an intercept). The firmness of a honeycomb Plastic solid becomes the outstanding thing, so that this apparent viscosity (firmness index viscosity) is large.
[0028] (Measuring method of the deficit number of a rib) The deficit number of the cel when extruding the honeycomb with a diameter of 100mm which has 62 square cel configurations /of 2 cm 100m by predetermined wall thickness was measured.
[0029] (Measuring method of grain size) It measured in the SEDI graph (X-ray sedimentation method) by the microphone ROMERI tick company.
[0030] (Measuring method of a BET specific surface area) It measured by flow SOBU II2300 (laser diffraction method) by the microphone ROMERI tick company (helium [30%] / N2 [70%] gas was used as adsorption gas).
[0031] (Measuring method of porosity) Porosity was converted from the total pore volume of a method of mercury penetration (cordierite true specific gravity was set to 2.52 at this time).
[0032] (Measuring method of thermal shock resistance) When the honeycomb structure object (honeycomb baking object) of a room temperature was fed into an electric furnace and it took out to a room temperature again after 30-minute maintenance, it measured whether there would be any destruction by tap tone judging (50-degree-C [600 degrees C to] step-up and a safe temperature [**] are displayed).
[0033] (Measuring method of eye SOSUTA tech reinforcement) The honeycomb structure object (honeycomb baking object) was inserted into the flexible tube, the equivalent pressure by water pressure was hung, and the pressure (kg/cm2) which produced partial destruction was measured (average of ten samples).
[0034] (Examples 1-8, examples 1-4 of a comparison) According to the preparation rate shown in Table 1 as a cordierite-ized raw material, it prepared, respectively, 4 % of the weight of methyl cellulose and addition water were added and kneaded to 100 % of the weight of raw materials, and it considered as the plastic matter in which extrusion molding is possible. The fluid measurement result of the obtained plastic matter is shown in Table 2.
[0035]
[Table 1]

	カオリンの特性			調合割合（重量%）							カオリン＋タルク＋水酸化アルミニウムの合計（重量%）	コージェライト化原料の合計（重量%）
	BET比表面積（m^2/g）	平均粒子径（μm）	平均粒径/BET	カオリン	タルクA	タルクB	仮焼カオリン	アルミナ	水酸化アルミニウム	シリカ		
実施例1	4	15	3.750	21	39	—	13	9	13	5	73	100
実施例2	6	11	1.833	21	—	39	13	9	13	5	73	100
実施例3	8	9	1.125	21	—	39	13	9	13	5	73	100
実施例4	10	10	1.000	21	—	39	13	9	13	5	73	100
実施例5	10	10	1.000	10	—	39	23	7	16	5	65	100
実施例6	8	9	1.125	34	—	39	7	11	7	2	80	100
実施例7	6	11	1.833	47	—	39	0	14	0	0	86	100
実施例8	5	5	1.000	21	—	39	22	5	13	0	73	100
比較例1	12	4	0.333	21	—	39	23	9	8	0	68	100
比較例2	6	11	1.833	7	—	40	26	9	13	5	60	100
比較例3	4	15	3.750	21	41	—	10	21	0	7	62	100
比較例4	6	11	1.833	21	—	39	13	9	13	5	73	100

[0036] The plastic matter which is each cordierite-ized raw material batch next, in a well-known extrusion method Predetermined wall thickness (refer to slit width of Table 2), the number of cels : Diameter:103mm which has 62 square cel configurations /of 2 cm, Height: After fabricating a 120mm cylindrical shape honeycomb structure object (honeycomb Plastic solid), it was made to dry and calcinated by 1420 degree-Cx4hr (temperature up temperature [average for 1100 - 1350 degrees C]:60 degree C/hr) (examples 1-8, examples 1-4 of a comparison). The firmness of the acquired honeycomb Plastic solid and the measurement result of the deficit number of a rib, and the measurement result of the coefficient of thermal expansion (the direction of passage of a honeycomb structure object) in 40-800 degrees C of the acquired honeycomb baking object (honeycomb structure object), porosity, thermal shock resistance, and AISO static reinforcement are shown in Table 2.

[0037]

[Table 2]

	コージェライト化原料の分級の有無	押出成形時の押出ダイスのスリット幅（μm）	ハニカム成形体特性			ハニカム焼成体特性			
			流動性（MPa・s）	保形性（MPa・s）	リブの欠損個数	熱膨張係数（10^{-6}/℃）[40-800℃]	気孔率（%）	耐熱衝撃性（℃）	アイソスタティック強度（kg/cm^2）
実施例1	有	110	5.8	70	0	0.8	38	750	70
実施例2	有	75	5.3	53	0	0.6	35	800	40
実施例3	有	75	5.6	56	0	0.5	30	825	45
実施例4	有	55	5.4	52	3	0.4	28	850	10
実施例5	有	110	5.5	40	0	0.35	28	825	50
実施例6	有	75	5.7	61	0	0.6	32	800	65
実施例7	有	75	6.1	59	0	0.65	36	775	30
実施例8	有	44	5.6	60	1	0.2	24	900	35
比較例1	有	90	5.5	35	0	0.4	20	825	6
比較例2	有	110	5.2	33	0	0.55	32	800	8
比較例3	有	180	5.6	38	0	1.0	40	650	6
比較例4	無	75	5.6	59	25	0.6	35	700	8

[0038] (Consideration: Examples 1-8, examples 1-4 of a comparison) Drawing 1 is a graph which shows the relation between the fluidity of the example 1 when adding water, an example 3, and the example 1 of a comparison, and firmness to a cordierite-ized raw material batch. The fluidity of a plastic matter examined

the value of firmness index viscosity in case fluid index viscosity is 5.5 MPa-s in consideration of the knockout speed at the time of honeycomb production, i.e., productivity. In addition, average wall thickness: It is known that the firmness index viscosity which a thin wall honeycomb 110 micrometers or less can fabricate good without faults, such as deformation, is 40 MPa-s. Here, since the following [more than mean-particle-diameter:5micrometer and BET specific surface area:10m2/g] were being used for an example 1 and an example 3, both firmness index viscosity in case fluid index viscosity is 5.5 MPa-s is 40 or more MPa-s, and the thin wall honeycomb not more than average wall thickness:110micrometer was formed with the sufficient yield good. Moreover, since the value of the mean particle diameter/BET specific surface area of a kaolin is large as compared with an example 3, the example 1 serves as a plastic matter which was further excellent in the moldability. Furthermore, since they were not got blocked in the slit of an extrusion dice by using the cordierite-ized raw material which classified under in the slit width of an extrusion dice while the following [more than mean-particle-diameter:5micrometer and BET specific surface area:10m2/g] are used for examples 1-8, they were able to acquire the good honeycomb Plastic solid which does not almost have the deficit of a rib.

[0039] On the other hand, since the mean particle diameter of a kaolin is [4 micrometers and a BET specific surface area] 12m2/g, the example 1 of a comparison firmness index viscosity in case fluid index viscosity is 5.5 MPa-s When it became 35 MPa-s and the thin wall honeycomb not more than average wall thickness:110micrometer was fabricated, deformation of a cel, the surface piece, the split, etc. occurred, a good Plastic solid could not be acquired, and productivity was not able to fall remarkably and was not able to obtain only 5kg/cm2 of hydrostatic-pressure disruptive strength. Since the addition of a kaolin was [the sum total of 7% and a cordierite metaplasia raw material] 60%, deformation of a cel, the surface piece, the split, etc. were able to occur in the honeycomb which 5.2 MPa-s and firmness index viscosity became 33 MPa-s, and the fluid index viscosity at the time of extrusion molding fabricated, and the example 2 of a comparison could not acquire a good Plastic solid, and was not able to obtain only 8kg/cm2 of hydrostatic-pressure disruptive strength. Since the sum total of a cordierite metaplasia raw material was 62%, deformation of a cel, the surface piece, the split, etc. were able to occur in the honeycomb which 5.6 MPa-s and firmness index viscosity became 38 MPa-s, and the fluid index viscosity at the time of extrusion molding fabricated, the example 3 of a comparison could not acquire a good Plastic solid, and only 6kg/cm2 of hydrostatic-pressure disruptive strength was not able to acquire it. Moreover, since a coefficient of thermal expansion was also 1.0x10-6/degree C, only 650 degrees C of averages of thermal shock resistance were not able to be acquired. Since the example 4 of a comparison did not classify the cordierite-ized raw material, during extrusion molding, the raw material particle of the coarse grain more than the slit width of an extrusion dice was got blocked in the slit of an extrusion dice, and 25 deficits had generated it to the rib of a honeycomb. For this reason, the reinforcement of a honeycomb deteriorated and only 8kg/cm2 of hydrostatic-pressure disruptive strength was not able to be obtained.

[0040]

[Effect of the Invention] As explained above, the manufacture approach of the nature of cordierite ceramic honeycomb structure object of this invention can be contributed to improvement in the formation of a thin wall of a nature of cordierite ceramic honeycomb structure object and the moldability at the time of extrusion molding (especially a fluidity and firmness), a mechanical strength (hydrostatic-pressure disruptive strength), and a catalyst support property while being able to form a high cel consistency.

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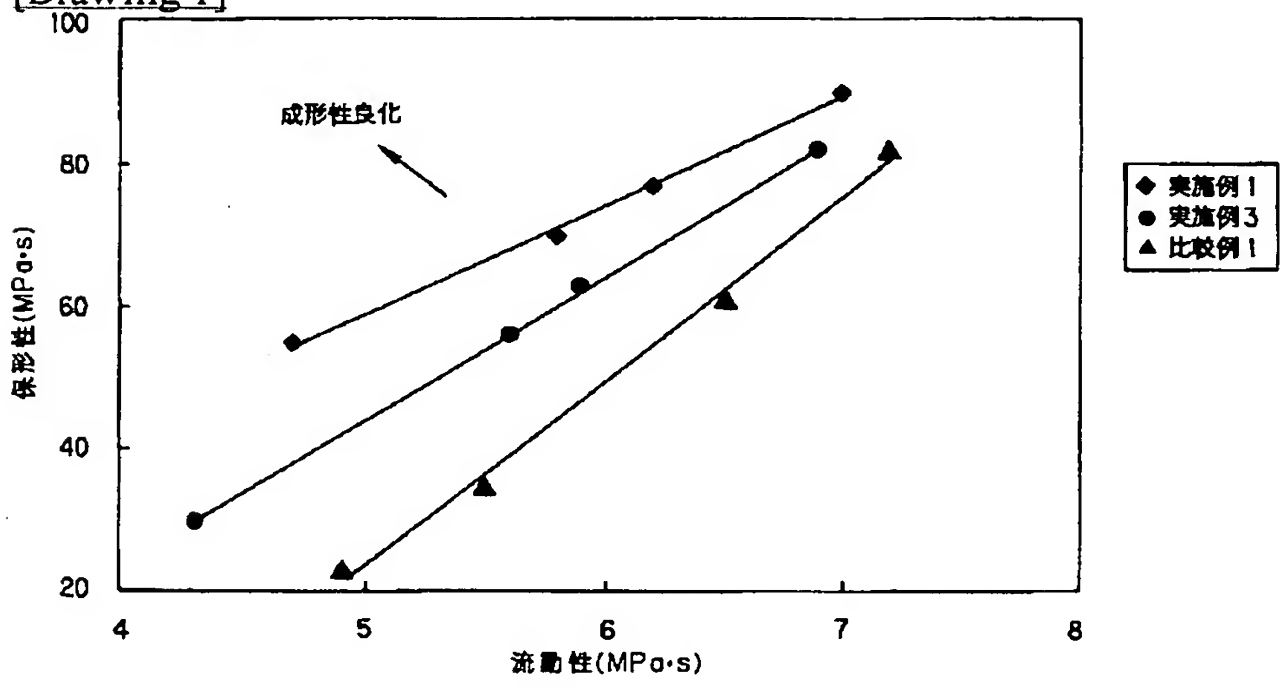
DRAWINGS

[Drawing 1]



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* NOTICES *

WRITTEN AMENDMENT

[Procedure revision]
[Filing Date] April 21, Heisei 12 (2000. 4.21)
[Procedure amendment 1]
[Document to be Amended] Specification
[Item(s) to be Amended] Claim 3
[Method of Amendment] Modification
[Proposed Amendment]
[Claim 3] The manufacture approach of the nature of cordierite ceramic honeycomb structure object according to claim 1 or 2 using the cordierite-ized raw material which classified under in the slit width of an extrusion dice in the cordierite-ized raw material batch.
[Procedure amendment 2]
[Document to be Amended] Specification
[Item(s) to be Amended] Claim 5
[Method of Amendment] Modification
[Proposed Amendment]
[Claim 5] The manufacture approach of a nature of cordierite ceramic honeycomb structure object given in any 1 term of claims 1-4 24 - 38% and whose AISO static reinforcement porosity is two or more 10 kgf/cm while the coefficient of thermal expansion for 40-800 degrees C of the direction of passage of a nature of cordierite ceramic honeycomb structure object is less than [0.8x10-6/degree C].
[Procedure amendment 3]
[Document to be Amended] Specification
[Item(s) to be Amended] 0019
[Method of Amendment] Modification
[Proposed Amendment]
[0019] Moreover, as for the cordierite-ized raw material batch used by this invention, it is desirable to use the cordierite-ized raw material which classified under in the slit width of an extrusion dice. It can prevent getting it blocked in the slit of an extrusion dice by this, and the good Plastic solid which does not have a deficit in the rib of a honeycomb can be acquired.
[Procedure amendment 4]
[Document to be Amended] Specification
[Item(s) to be Amended] 0023
[Method of Amendment] Modification
[Proposed Amendment]
[0023] Since the plastic matter which was excellent in the fluidity at the time of extrusion molding by carrying out specified quantity (10 % of the weight or more) combination of the kaolin whose mean particle diameter is 5 micrometers or more, and whose BET specific surface area is below 10m2/g at this time, and also has the firmness over the self-weight deformation after extrusion molding is obtained, a thin wall and the honeycomb structure object of a high cel consistency (for example, wall thickness: 40 micrometers, cel consistency:200 cel / cm2) can be manufactured. Moreover, while there are very few coefficients of thermal expansion of the honeycomb baking object after cel deformation of the honeycomb Plastic solid after extrusion molding and baking by manufacturing a thin wall honeycomb structure object as mentioned above and being able to make AISO static reinforcement in the honeycomb baking object of 24 - 38% of porosity into two or more 10 kgf/cm, when porosity is 30% or more, a catalyst support property can also be raised.
[Procedure amendment 5]

[Document to be Amended] Specification
[Item(s) to be Amended] 0033
[Method of Amendment] Modification
[Proposed Amendment]
[0033] (Measuring method of AISO static reinforcement) The honeycomb structure object (honeycomb baking object) was inserted into the flexible tube, the equivalent pressure by water pressure was hung, and the pressure (kgf/cm2) which produced partial destruction was measured (average of ten samples).
[Procedure amendment 6]
[Document to be Amended] Specification
[Item(s) to be Amended] 0036
[Method of Amendment] Modification
[Proposed Amendment]
[0036] The plastic matter which is each cordierite-ized raw material batch next, in a well-known extrusion method Predetermined wall thickness (refer to slit width of Table 2), the number of cels : Diameter:103mm which has 62 square cel configurations /of 2 cm, Height: After fabricating a 120mm cylindrical shape honeycomb structure object (honeycomb Plastic solid), it was made to dry and calcinated by 1420 degree-Cx4hr (programming-rate [average for 1100 - 1350 degrees C]:60 degree C/hr) (examples 1-8, examples 1-4 of a comparison). The firmness of the acquired honeycomb Plastic solid and the measurement result of the deficit number of a rib, and the measurement result of the coefficient of thermal expansion (the direction of passage of a honeycomb structure object) in 40-800 degrees C of the acquired honeycomb baking object (honeycomb structure object), porosity, thermal shock resistance, and AISO static reinforcement are shown in Table 2.
[Procedure amendment 7]
[Document to be Amended] Specification
[Item(s) to be Amended] 0037
[Method of Amendment] Modification
[Proposed Amendment]
[0037]
[Table 2]

	コージェライト化原料の分級の有無	押出成形時の押出ダイスのスリット幅(μm)	ハニカム成形体特性			ハニカム焼成	
			流動性 (MPa・s)	保形性 (MPa・s)	リブの欠損個数	熱膨張係数 (10^{-6}/℃) [40-800℃]	気孔率 (%)
実施例1	有	110	5.8	70	0	0.8	38
実施例2	有	75	5.3	53	0	0.6	35
実施例3	有	75	5.6	56	0	0.5	30
実施例4	有	55	5.4	52	3	0.4	28
実施例5	有	110	5.5	40	0	0.35	28
実施例6	有	75	5.7	61	0	0.6	32
実施例7	有	75	5.1	59	0	0.65	36
実施例8	有	44	5.6	60	1	0.2	24
比較例1	有	90	5.5	35	0	0.4	20
比較例2	有	110	5.2	33	0	0.55	32
比較例3	有	180	5.6	38	0	1.0	40
比較例4	無	75	5.6	59	25	0.6	35

[Procedure amendment 8]
[Document to be Amended] Specification
[Item(s) to be Amended] 0039
[Method of Amendment] Modification
[Proposed Amendment]
[0039] On the other hand, since the mean particle diameter of a kaolin is [4 micrometers and a BET specific surface area] 12m2/g, the example 1 of a comparison firmness index viscosity in case fluid index viscosity is 5.5 MPa-s When it became 35 MPa-s and the thin wall honeycomb not more than average wall thickness:110micrometer was fabricated, deformation of a cel, the surface piece, the split, etc. occurred, a good Plastic solid could not be acquired, but productivity was not able to fall remarkably and hydrostatic-pressure disruptive strength was also able to obtain only 5 kgf/cm2. Deformation of a cel, the surface piece, the split, etc. were able to occur in the honeycomb which 5.2 MPa-s and firmness index viscosity became 33 MPa-s, and the fluid index viscosity at the time of extrusion molding fabricated since the addition of a kaolin was [the sum total of 7% and a cordierite metaplasia raw material] 60%, and the example 2 of a comparison could not acquire a good Plastic solid, but hydrostatic-pressure disruptive strength was also able to obtain only 8 kgf/cm2. Deformation of a cel, the surface piece, the split, etc. were able to occur in the honeycomb which 5.6 MPa-s and firmness index viscosity became 38 MPa-s, and the fluid index viscosity at the time of extrusion molding fabricated since the sum total of a cordierite metaplasia raw material was 62%, and the example 3 of a comparison could not acquire a good Plastic solid, but hydrostatic-pressure disruptive strength was able to obtain only 6 kgf/cm2. Moreover, since a coefficient of thermal expansion was also 1.0x10-6/degree C, only 650 degrees C of averages of thermal shock resistance were not able to be acquired. Since the example 4 of a comparison did not classify the cordierite-ized raw material, during extrusion molding, the raw material particle of the coarse grain more than the slit width of an extrusion dice was got blocked in the slit of an extrusion dice, and 25 deficits had generated it to the rib of a honeycomb. For this reason, the reinforcement of a honeycomb deteriorated and only 8 kgf/cm2 was able to obtain

hydrostatic-pressure disruptive strength.

[Translation done.]